PB88-123971

Environmental Protection Agency Research in Hazardous Waste Volume Reduction

(U.S.) Environmental Protection Agency
Cincinnati, OH

Oct 87

U.S. Department of Commerce
National Technical Information Service
NTIS

PB88-123971

EPA/600/D-87/328
October 1987

ENVIRONMENTAL PROTECTION AGENCY RESEARCH IN HAZARDOUS WASTE VOLUME REDUCTION

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-87/328		PB88 123971/AS

4. TITLE AND SUBTITLE	5. REPORT DATE
Environmental Protection Agency Research in Hazardous Waste Volume Reduction	Oct. 1987
	6. PERFORMING ORGANIZATION CODE: USEPA/HWERL

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
J.F. Martin, M.J. Stutsman & E. Grossman III	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Hazardous Waste Engineering Research Laboratory U.S. EPA Cincinnati, OH 45268	11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Hazardous Waste Engineering Research Laboratory U.S. EPA Cincinnati, OH 45268	Symposium Paper
	14. SPONSORING AGENCY CODE: EPA 600/ 12

15. SUPPLEMENTARY NOTES

16. ABSTRACT

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A phosphate precipitation process has been shown to be effective in selectively removing metals from metal finishing sludge materials. Research also indicates that sodium smectite clays, an abundant natural material, can be modified in structure so that they have excellent adsorptive properties for removing compounds like benzene, trichlorophenol, and pentachlorophenol from aqueous solutions. The separation of dilute hazardous organics utilizing thin-film, composite, aromatic polyamide membranes also appears to be advantageous in terms of high solute separation at low pressures (1-2 MPa) and broad pH operating ranges (pH 2-12).

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	20
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE $12.95 / MF 6.95

EPA Form 2220-1 (9-73)

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency. It has been subject to the Agency's peer and administrative review. and it has been approved for publication as an EPA document.

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ABSTRACT

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A phosphate precipitation process has been shown to be effective in selectively removing metals from metal finishing sludge materials. Research also indicates that sodium smectite clays, an abundant natural material, can be modified in structure so that they have excellent adsorptive properties for removing compounds like benzene, trichlorophenol, and pentachlorophenol from aqueous solutions. The separation of dilute hazardous organics utilizing thin-film, composite, aromatic polyamide membranes also appears to be advantageous in terms of high solute separation at low pressures (1-2 MPa) and broad pH operating ranges (pH 2-12).

INTRODUCTION

Within the Hazardous Waste Engineering Research Laboratory, the Chemical and Biological Detoxification Branch conducts research on emerging technologies to provide alternative options for treating hazardous wastes. Emphasis is placed on developing new and innovative methods for treating wastes not easily handled by existing technology. These research efforts support EPA's regulatory programs as well as Regional Office and State decisions regarding treatment alternatives, R&D permits and remedial actions. The research is categorized in three principal areas: (1) Physical/Chemical Treatment, (2) Chemical Dehalogenation/Detoxification, and (3) Biological Treatment.

The physical/chemical treatment technology portion of the program specifically addresses dilute aqueous wastes and metal bearing wastes that are not suitable for land disposal. This technology is also applicable to leachates and large volumes of surface water and groundwater encountered in the clean-up of EPA Superfund sites. It is cost prohibitive to incinerate high volume aqueous waste streams while other currently available treatment techniques may be applied only at considerable cost and with varying degrees of success. Research in this area is designed to develop and demonstrate new methods for extracting organic and inorganic contaminants from dilute aqueous waste streams and sediments, for concentrating large volumes of aqueous wastes, and for removal and recovery of metal ions from a variety of waste matrices. New techniques and treatment schemes that are not commercially available or in use for hazardous wastes must be proven and tested for both the user and the regulator. The primary benefit gained is more cost-effective treatment of hazardous waste by eliminating the need to treat massive amounts of water, and by developing recycle and reuse options such as those applicable to both large and small

electroplating and metal finishing shops. Four examples of research undertaken through this program are addressed below.

SELECTIVE METAL RECOVERY

Process wastewaters from the metal finishing industry often contain cyanides and heavy metals which have a detrimental effect on the environment if directly discharged. Such discharges are regulated by Federal, State, or local laws which may require pretreatment such as chemical oxidation (or reduction), neutralization, and precipitation to destroy cyanide and remove heavy metals as hydroxide sludges. These sludges have traditionally been disposed in landfill sites, however, recovery of heavy metals from metal finishing sludges can provide for conservation of energy and metal resources while reducing disposal problems. Research at the Montana College of Mineral Science and Technology (Montana Tech) has produced a procedure for treating metal-bearing sludges via hydrometallurgical techniques to recover and isolate valuable metal resources. The treatment of hydroxide sludges for metal value recovery will produce several beneficial results: economic benefits from the metal recovered will help offset the cost of recovery/treatment; non-renewable resources will be recycled for use by society; and there will be significantly less hazardous material to be disposed.

Experimental work on recovery of specific metals from mixed metal hydroxide sludges was accomplished by Montana Tech in three phases. The third phase results have been fully documented in a draft final report submitted to EPA by Montana Tech and are briefly summarized below. The first phase of the study concentrated on developing preliminary flowsheets for the separation and recovery of metal values from mixed metal sludge materials, performing laboratory

studies to test the applicability of the preliminary flowsheets, developing a test assembly of unit operations capable of treating 34-45 kg (75-100 pounds) of sludge per day, and conducting shakedown exercises of the test assembly to delineate conditions for successful operation and/or to note potential operational problems.

The second phase of research concentrated on investigating potential alternative unit operations identified in Phase I, further testing the assembly developed in Phase I, developing long-term continuous test data for the unit operations, and delineating potential process and materials handling problems. The results of the Phase I and Phase II studies are provided in EPA Report 600/2-85/128 "Metal Value Recovery from Metal Hydroxide Sludges", March 1985 (PB86 157294/AS).

The third phase of the investigation concentrated on developing an improved flowsheet to separate and recover metal values from electroplating sludge materials, collecting bench-scale experimental data to verify the feasibility of the proposed flowsheet, demonstrating the effectiveness of the separation techniques on a large scale (34-45 kg of sludge per day), and developing a first order economic evaluation of the proposed flowsheet for an exemplary centralized treatment facility.

Although effective and selective separation of metals (Fe, Cu, Zn, Cr, and Ni) from complex mixed metal solutions had already been accomplished, the unit operations for removal of iron and oxidation and recovery of chromium were high in cost and energy requirements. Emphasis was directed therefore toward investigating the application of phosphate precipitation as a means of selectively separating iron and chromium from divalent cation species. Bench-scale test work showed that trivalent cations can be very effectively stripped from solu-

tions in preference to divalent cations under low pH and room temperature conditions by phosphate precipitation. The successful application of simple precipitation of iron and chromium from mixed solutions could mean elimination of two high cost unit operations:

1. Iron removal by jarosite precipitation;
2. Chromium recovery by oxidation to chromate.

A large data base was generated during the course of the study for both bench-scale and large-scale test work. The bench-scale study results support the following conclusions:

1. Trivalent cations can be effectively and selectively separated from divalent and monovalent solution species.
2. Ferric iron concentrations can be lowered to a few mg/liter in acidic solutions.
3. Ferric phosphate precipitation is rapid and selective over trivalent chromium and divalent cations under room temperature conditions.
4. Ferric phosphate precipitates as small spherites showing excellent filtering characteristics.
5. Ferric phosphate precipitates in a similar manner from acidic solutions under essentially the same experimental conditions regardless of the solvent matrix, e.g., from sulfate, chloride, nitrate or ammonium solutions.
6. Ferric phosphate can be converted to ferric hydroxide with the regeneration of the phosphate reagent by a caustic leach.
7. Chromium phosphate precipitation requires an incubation time of several hours at room temperature but is very rapid at elevated temperatures.

8. Filterability of chromium phosphate (small spherites) precipitated at an elevated temperature is about the same as the filterability of ferric phosphate.

9. Chromium phosphate can be converted to marketable products by a soda ash roast process producing metal chromates or chromic acid.

The objective of the large-scale test work was to demonstrate that selective separations could be accomplished on a significant quantity of actual sludge material The large-scale test work confirmed the bench scale results. Important conclusions that have resulted include:

1. Sulfuric acid leaching is effective in redissolving metals from electroplating sludge. In the case of electromachining sludge, the leach residue contained most of the niobium and titanium and, therefore, provided a valuable recoverable residue.

2. The weight of solids that must be discarded following metal recovery operations, including the leach residue and converted ferric phosphate (to ferric hydroxide), is less than the weight of the starting sludge. Both the leach residue and iron precipitate solids pass EPA's TCLP extraction test and can normally be disposed in non-hazardous disposal sites.

3. The metal products that are recovered are of sufficient purity to serve as feedstock for commercial uses or for conversion to other more marketable products.

MODIFIED CLAYS AS ADSORPTION MEDIA

Clay is an abundant natural material which can be modified so that it will adsorb organic pollutants. Sodium smectite clay, for example, consists of a

layered structure containing sodium ions between the negatively charged layers. This material is hydrophilic and not very adsorbent to organics. All of the modifications to clay involve replacing that sodium ion by ion exchange with another ion which converts the clay into a material that is adsorbent to organic pollutants.

EPA is sponsoring research into modified clays as adsorbents for treatment of organic pollutants at Michigan State University and at the University of Michigan (Cooperative Agreements CR813215 and CR813028). The following is a summary of several of the techniques and approaches being investigated at Michigan State University. For detailed technical descriptions and results the reader is referred to the published papers prepared by these universities. EPA will publish project summaries and reports upon completion of the ongoing technical efforts.

One clay modification which is being investigated is the substitution of copper ions (Cu^{++}) for the sodium ions in the naturally occurring smectite clay. The objective is to use the copper ions in the modified smectite clay to oxidize organic species to form radical cations (when water is absent). The radical cations will be subject to dechlorination and polymerization reactions which convert the original pollutants into products of lower toxicity which are easier to treat and dispose. It was found that the radical cation reactions observed required the presence of the Cu (II) smectite and would not occur with copper alone.

When Cu (II) smectite was refluxed at $69^{o}C$ in a solution of pentachlorophenol, 4-chlorophenol or 3-chloroanisol in n-hexane, the normal light blue color of the clay was replaced by a deep color, indicating the presence of the organic radical. An electron is transferred from the organic molecule reducing

the Cu (II) to Cu (I) and producing the radical cation. Electron spin resonance was used to demonstrate the formation of radical cations for pentachlorophenol, 4-chlorophenol and 3-chloroanisol. The pentachlorophenol and 3-chloroanisol radicals formed dimers as revealed by mass spectroscopy; the 3-chlorophenol radicals formed dimers as observed by changes in the UV spectrum. Pentachlorophenol was dechlorinated to 2,3,5,6-tetrachlorophenol.

When 4-chloroanisol is reacted with Cu (II) smectite in hexane at reflux temperatures, a blue colored clay-organic complex containing the organic radical is formed. Reaction of this colored material with methanol results in the disappearance of the color and formation of the dechlorinated dimer product, 4,4'-dimethoxybiphenyl. Chloride ion is recovered from the methanol extract.

Reaction of trichloroethylene and Cu(II)smectite in n-hexane at reflux temperatures also shows the radical formation, polymerization and dechlorination of the trichloroethylene molecule. Mass spectroscopy indicates molecular weights of 500 and polymers of 2 to 5 or more multiples of the monomer. The resulting polymer is either dechlorinated or contains greatly reduced chlorine. The chlorinated positions are replaced by oxygenated positions, OH or =O.

A second type of clay modification also being studied is the organo clay. Several clay-organic complexes were synthesized by placing quaternary ammonium cations on smectite by cation exchange. When a small cation such as tetramethyl ammonium is placed on the clay, the clay becomes organophilic and acts as a conventional adsorbent of organics in aqueous solutions. It is also an efficient adsorber for benzene but not for pentachlorophenol or dichlorobenzene. If a large cation with a long carbon chain such as hexadecyltrimethyl ammonium is used, the chains interact giving the clay characteristics of an organic

solvent. This organo clay will partition trichloroethylene and benzene and behaves similar to a solvent like hexane in its partitioning characteristics.

The third type of clay modification being studied is the pillared/delaminated structure. Smectite clay is pillared by substituting hydroxyaluminum into the clay by cation exchange, creating a stable compound which contains pores between the mineral layers. Delaminated clays are also being prepared which are chemically identical to the pillared clays but contain macroporosities because of the many irregularities and frequent edge-to-face positioning of the mineral layers. These structures are currently being evaluated for their ability to adsorb chlorinated organics from aqueous solution.

REVERSE OSMOSIS MEMBRANE PROCESSES

For hazardous wastes containing priority organics and salts, such as aqueous wastes contained at industrial plants, abandoned manufacturing sites and Superfund sites, reverse osmosis membranes can provide simultaneous separation of both organics and inorganics. The industrial development of non-cellulosic, (aromatic polyamide, sulfonated polysulfone, etc.) thin-film, composite membranes has provided a means for reverse osmosis treatment with high solute separations and minimal compaction problems.

Use of this low pressure process to concentrate selected priority pollutants from hazardous wastes will substantially improve conventional destruction techniques. Previous and current work, conducted at the University of Kentucky, deals with the use of thin-film, composite membranes for concentration and separation of pollutants from aqueous waste streams. Spiked waste streams utilized to date include: PAH compounds, phenol, chloro- and nitrophenols, chlorinated benzenes, phthalates and heavy metals. An actual waste

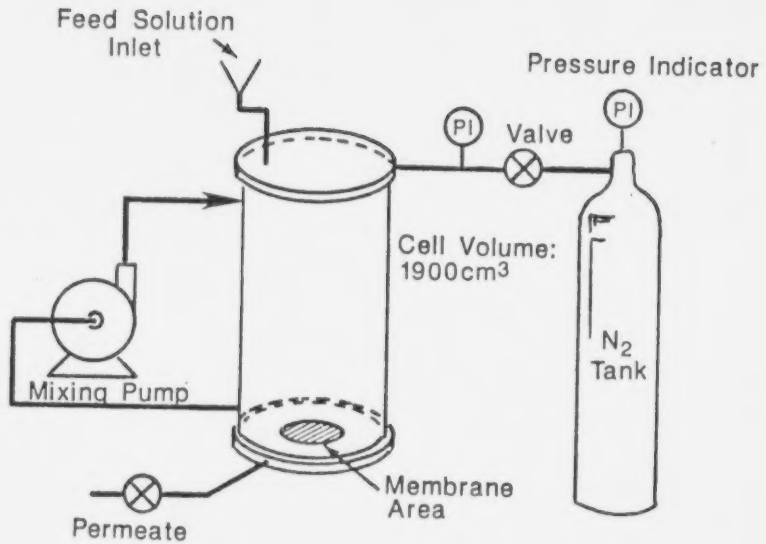

Figure 1. Batch Membrane Unit.

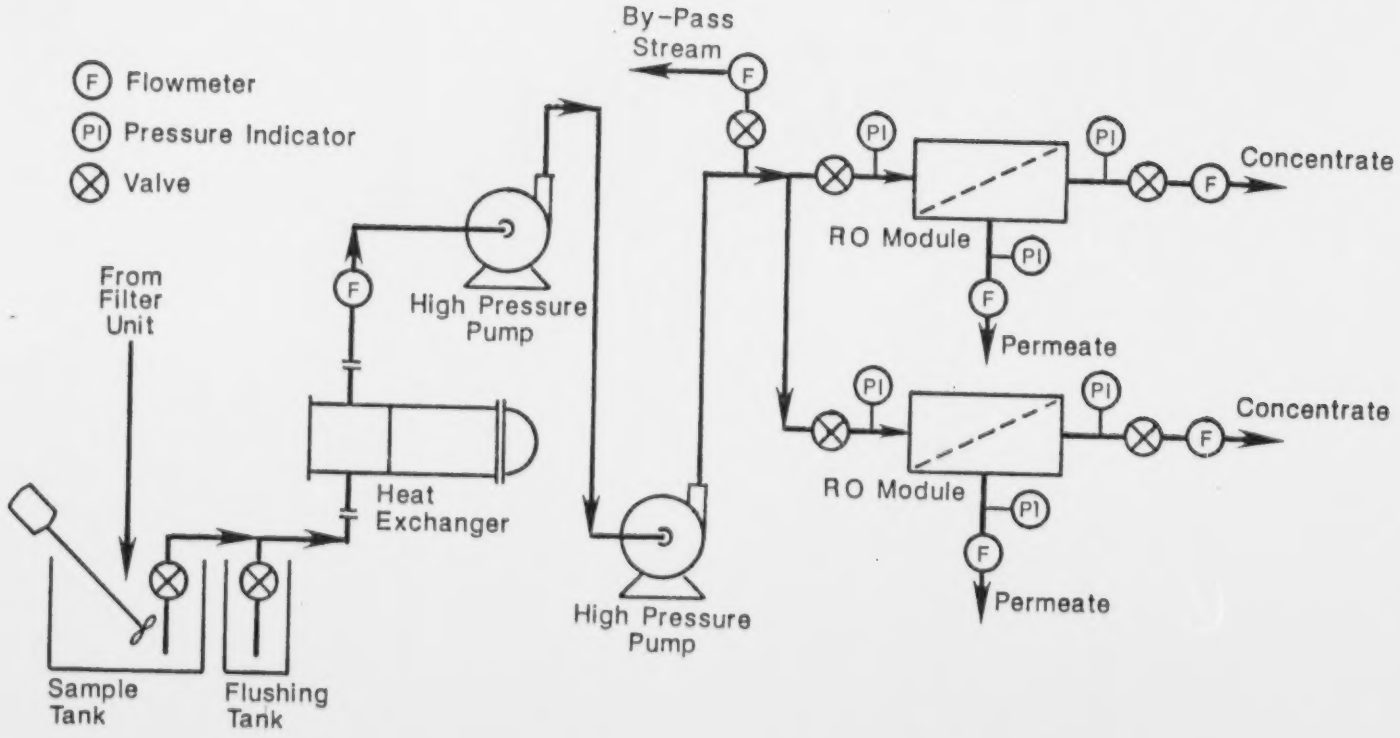

Figure 2. Membrane Flow Diagram of The Continuous Unit Operation.

stream from a wood treating site was also collected for treatment in the membrane system. Separation of pollutants and operation of the membrane system were evaluated as a function of system pressure, flow rate, and input waste concentration.

Membrane studies were conducted in batch, continuous thin channel, and continuous spiral-wound modules (Figures 1 & 2). The batch operating conditions were 1400-1800 ml of feed solution, a system pressure (ΔP) of 1.38-2.07 MPa (200-300 psi) and pH = 4.5 - 11.8. The continuous unit operating conditions were: ΔP = 0.69 - 2.07 MPa (100-300 psi), Reynold's number (Re) = 4000 - 9000, and pH = 3.3 - 11.8. For both the batch and continuous systems, standard distilled water flux and salt (NaCl) rejection were obtained prior to experiments with any hazardous organic compounds. The membranes used were made of aromatic polyamide.

The batch cell portion of the study focused on the mixtures of selected chlorophenols and nitrophenols. One run involving phenol and a salt mixture was also conducted. For chloro- and nitrophenols, a wide range of pH values was selected in order to establish the rejection behavior of non-ionized and ionized species. Membrane stability for both the continuous and batch units was checked with standard NaCl runs and with distilled water. The membrane showed a 15% drop in distilled water flux with standard NaCl rejections remaining constant at 97-98%, indicating good membrane stability.

Separation of naphthalene (solubility 20-22 mg/l), anthracene (solubility 0.12 mg/l), phenanthrene (solubility 0.58 mg/l), and dimethylphthalate (solubility 278 mg/l) was carried out in the batch cell. Rejection of dimethylphthalate was about 97%, and rejection of naphthalene was 98.0%. For the higher molecular weight anthracene and phenanthrene, which are chemically

similar to naphthalene, the rejections were 98-99%. The flux drops with these compounds were only 3-5%. The material balance analysis of PAH compounds showed significant loss of these compounds through the test, probably due to adsorption on the membrane.

Additional experimental runs were performed on mixtures of chlorophenols (phenol, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), and 4-chlorocresol (4-CCR)), and nitrophenols (phenol, 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP)). It is important to emphasize at this point that phenolics are ionizable species. As such, the pH values of various mixtures were varied from pH = 4.5 to pH = 11.8 to observe the separation characteristics at various ionization conditions. At solutions pH > 11 essentially all species are 100% ionized.

Experimental runs involving chlorophenol mixtures were performed at pH values of 5, 9, and 11. In each experimental run involving high pH, there was a smaller drop in permeate flux than in low-pH runs. The rejection of the individual species increases with pH value and with each chloro substitution on the phenol molecule. Similar runs with nitrophenol mixtures at high pH (pH = 11.5) showed very high rejections of phenol (98.3%), 2-NP (99.3%), and 4-NP (99.1%).

The chlorinated benzenes were run in the batch cell as mixtures of chlorobenzene (CB), 1,4-dichlorobenzene (1,4-DCB), and 1,2,4-trichlorobenzene (1,2,4-TCB). Similar mixtures were tested under stirred and quiescent conditions. Both tests were taken to at least 80% recovery of the feed solution and both showed rejections ranging from 67.6 to 99.7%.

Experiments with contaminated water from a wood processing plant were conducted in the batch reactor at pH 7 and at pH 11. The various phenol and

PAH compounds in the wastewater performed quite similarly to the compounds tested in the synthetic waste mixtures. Total rejection of organics in the waste stream ranged from 85% to 97%.

Tests of the continuous flow units were made with chloro- and nitrophenol mixtures in the turbulent flow regime. High flux drop was observed under non-ionization conditions (pH = 3.3) of the various solutes. These results were obtained even under a high Reynolds number (9000) and were similar to behavior observed in the batch cell.

To establish the flux drop and rejection phenomena, various types of mixtures were run using continuous flow, thin channel cells. Runs were conducted with mixtures of phenol, 2-CP, 2,4-DCP and 4-CCR containing a total molar concentration of 1.8 mM. At 300 psi the flux drop was 31%. With 2,4,6-TCP in the mixture the flux drop was 48%. A solution containing only 2,4,6-TCP (1.6 mM) indicated a flux drop of 35%. The flux behavior of the chlorophenol mixture containing phenol, 2-CP, 2,4-DCP, and 4-CCR, over the range 0.69 - 2.07 mPa (100 psi - 300 psi) was linear with ΔP, thus indicating the absence of surface polarization phenomena.

As noted previously, the University of Kentucky is continuing to study thin-film, composite membrane systems for separation of organics. Future studies will also involve utilization of charged membranes and processing of ozonated waste streams.

KEYWORDS

Hazardous waste, reverse osmosis, smectite clay, metals, waste treatment, metal recovery, aqueous waste.

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